

PCT

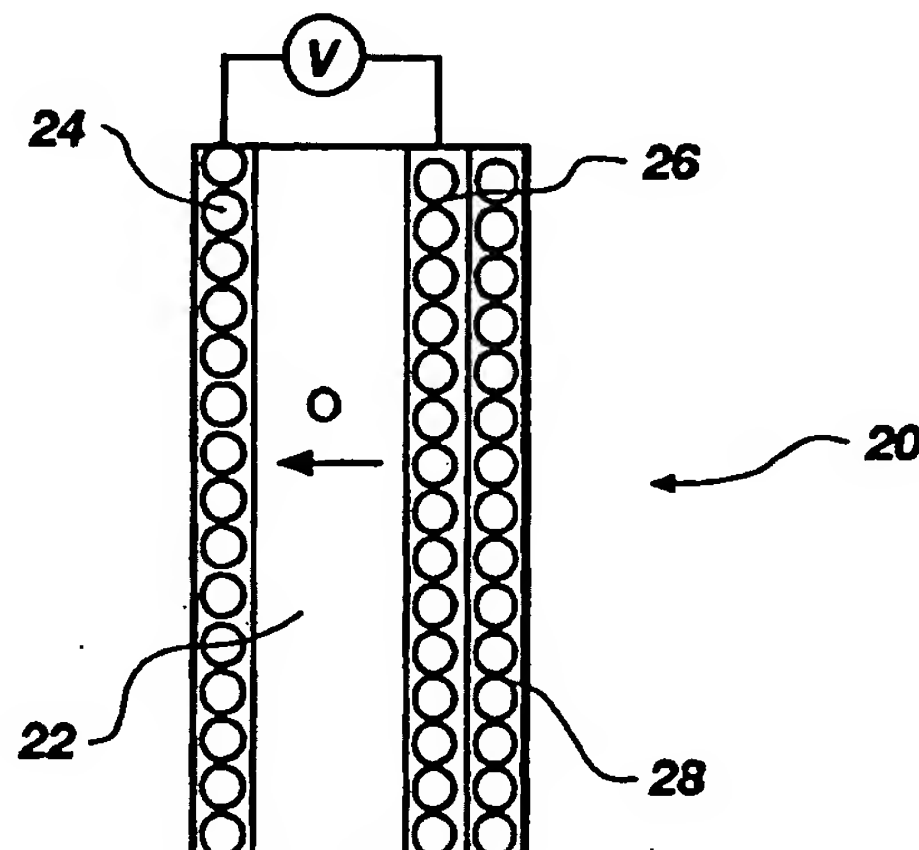
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁵ : C25B 1/00, 1/02, 9/00, 11/00, 11/02, 11/04, 11/06, 11/08, 13/04, G01N 27/26</p>	<p>A1</p>	<p>(11) International Publication Number: WO 94/25642 (43) International Publication Date: 10 November 1994 (10.11.94)</p>
<p>(21) International Application Number: PCT/US94/04525 (22) International Filing Date: 26 April 1994 (26.04.94) (30) Priority Data: 054,159 26 April 1993 (26.04.93) US (71) Applicant: CERAMATEC, INC. [US/US]; 2425 South 900 West, Salt Lake City, UT 84119 (US). (72) Inventors: LIU, Meilin; 1346 East 4170 South, Salt Lake City, UT 84124 (US). ZHU, Jiemin; Apartment #4, 3833 South 300 East, Salt Lake City, UT 84115 (US). JOSHI, Ashok, V.; 2845 East 3365 South, Salt Lake City, UT 84109 (US). (74) Agents: BOND, Laurence, B. et al; Trask, Britt & Rossa, P.O. Box 2550, Salt Lake City, UT 84110 (US).</p>		<p>(81) Designated States: JP, NO, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i></p>

(54) Title: ELECTROCHEMICAL CATALYTIC REDUCTION OF NO_x IN AN O₂-CONTAINING EXHAUST EMISSION



(57) Abstract

Disclosed are a process and an apparatus (20) for removing NO_x in an O₂-containing exhaust emission based on an electrochemically catalytic reduction process. Advantages to the electrochemically catalytic reduction process include high NO_x conversion efficiency and suitability for the removal of NO_x from the O₂-containing exhaust of mobile combustion sources due to the simplicity in construction, maintenance and operation where chemical-reducing agents are not required.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

ELECTROCHEMICAL CATALYTIC REDUCTION OF NO_x IN AN O₂-CONTAINING EXHAUST EMISSION

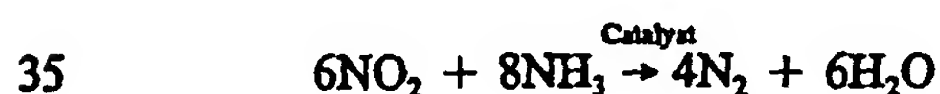
Technical Field: The invention relates to a method and apparatus for
5 reducing NO_x in exhaust emissions.

Background: Although nitric oxides are thermodynamically unstable
relative to their molecular elements, it is kinetically difficult to decompose the
compounds. Thus, the removal of the toxic and polluting nitrogen oxides
("NO_x") from emission of combustion sources, nitric plants, or other chemical
10 processes, has been investigated under various conditions, including thermal,
chemical, photo, and electrochemical reduction in the presence of catalysts. To
date, numerous chemical reducing agents (e.g., CO, NH₃, H₂, CH₄, etc.) and
catalysts (e.g., noble metals, pure and mixed metal oxides) have been introduced
to enhance the kinetics of NO_x decomposition.

15 Chemical processes based on catalysts and chemical-reducing agents have
seen commercial applications in large-scale removal of NO_x from stationary
combustion sources and nitric plants. However, the efficient removal of this
pollutant from mobile combustion sources remains an environmental problem.
One purpose of this invention is to explore avenues through which the NO_x
20 emitted from O₂-containing gas-fired engines can be successfully removed
without introducing chemical-reducing agents.

In the late seventies and early eighties, the electrochemical reduction of
NO_x was actively pursued. Most of the work concentrated on blackened
zirconia electrolyte with noble metal electrode. A problem with such an
25 approach is the low conversion level due to the fact that the noble metals (such
as platinum and gold) not only adsorb NO_x, but also actively adsorb other
reducible gas species, particularly oxygen, in the exhaust gas stream.

A successful chemical technique to remove NO_x in oxygen-containing
environments is the so-called Selective Catalytic Reduction (SCR) of NO_x with
30 NH₃:



-2-

Supported vanadium oxide (V_2O_5) is one of the best catalysts for SCR because of its high resistance to poisoning by sulphur oxides. It has been shown that the catalytic reactions are essentially a redox reaction of 5 valent and 4 valent vanadium.

5 For the removal of NO_x from emissions of mobile combustion sources (such as diesel engines), however, the injection of a chemical-reducing agent is very inconvenient and an alternative process which selectively reduces NO_x and requires no chemical-reducing agent would be an improvement in the art.

10 DISCLOSURE OF THE INVENTION

The invention includes an electrochemical process for separating NO_x from a O_2 -containing gas stream and converting the separated NO_x to elemental nitrogen and oxygen, without using chemical-reducing agents and using minimal energy consumption. To accomplish this, an electrochemical cell is provided
15 having catalytically-active electrodes and a solid oxide electrolyte. The NO_x -containing gas stream is brought into contact with a cathode and reduced to nitrogen and oxygen ions. The oxygen ions migrate to an anode where they are oxidized to form elemental oxygen.

The invention is useful for, among other things, the removal of NO_x
20 from the flue gases of a combustion process, whether the process is associated with the combustion of diesel, gasoline, LPG, coal, or other hydrocarbon fuel.

BRIEF DESCRIPTION OF THE FIGURES

In the drawings, which depict presently preferred embodiments of the
25 invention and in which like reference numerals refer to like parts in different views:

FIG. 1 is a schematic representation of an electrochemical cell for NO_x reduction in an oxygen-containing exhaust emission.

FIG. 2 depicts schematically an NO_x removal device utilizing the
30 electrochemical cell of FIG. 1.

FIG. 3 is a graph showing the corresponding power consumption (BHH/g) of the NO_x -reducing activity of the electrochemical cell identified in

-3-

FIG. 1 and used in a device identified in FIG. 2 at varied voltage with a low O₂ concentration gas stream.

FIG. 4 is a graph showing the corresponding power consumption (HH/g) of the device for NO_x-reduction at varied applied voltages under low O₂ concentration.

FIG. 5 is a graph depicting the percentage of NO_x converted with varying applied voltages of a device built according to the invention.

FIG. 6. is a graph showing the power used per gram of NO at various applied voltages and at varying oxygen concentrations.

FIG. 7 is a graph depicting the percentage of NO_x converted with varying applied voltages of a device built according to the invention at varied oxygen concentrations.

FIG. 8 is a graph showing the NO_x conversion performance of the device at various gas temperatures.

BEST MODE OF THE INVENTION

As shown in FIG. 1, an electrochemical cell for NO_x removal, generally 20, includes a solid oxide electrolyte 22 with a porous anode 24 and porous cathode 26 at opposite sides of the electrolyte 22. In a tubular electrochemical cell, the "sides" can be an inside and an outside. The electrolyte 22 preferably comprises an 8 mole percent yttria stabilized zirconia membrane 0.5 mm thick. The cathode 26 is a highly porous, gas-diffusion catalyst, such as supported vanadium oxides (e.g. U₂O₅ or V₂O₅) and other transition metal oxides. Abutting the cathode is an electron collecting layer 28 (e.g. a conductive perovskite-type oxide) which enhances the electrical conductivity of the resistive cathode 26. A highly porous, gas-diffusion electrode or anode 24 contacts the electrolyte membrane 22 on the other side. The anode 24 is preferably silver or another metal which is electrically conductive and chemically stable under the operating conditions.

As shown in FIG. 2, an electrochemical cell is incorporated into an NO_x removal device, generally 30. The electrochemical cell 20 is preferably supported by a porous metal grid 32 contained within a grid supporter 34. The

-4-

electrochemical cell 20, porous metal grid 32, and grid supporter 34 are contained within an air-tight reactor 36A, 36B forming a reaction chamber 38.

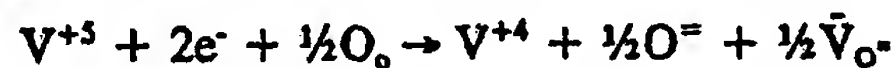
Gas feeds into the reaction chamber 38 through gas inlet 40. Reacted gas leaves the reaction chamber 38 via gas outlet 42. Inside the gas inlet is a thermocouple 44. Heating elements 46A, 46B are preferably placed outside of the reaction chamber 38 proximate the electrochemical cell 20. Electrical power is supplied to the porous metal grid 32 either from a battery, generator, alternator or other source.

The electrodes 24, 26 of the electrochemical cell 20 are catalytically-active. A NO_x -containing gas stream is fed in through the gas inlet 40 where it contacts the cathode 26 and is reduced to nitrogen and oxygen ions. The oxygen ions migrate to the anode 24 where they are oxidized to form elemental oxygen.

Two porous metal grids 32 held by two ceramic supporters 34 contact the electron collector layer 28 in cathode side and metal layer in anode side, respectively (FIG. 2).

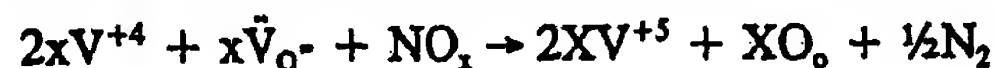
In operation, a gas stream containing NO_x is directed through inlet port 40 into the first region where it contacts the cathode 26. Voltage is applied through the metal grids from an external power source. The metal grids are preferably welded with two silver wires, and between the cathode 26 and anode 24.

The NO_x diffuses into the gas/cathode/electrolyte three-phase region and, under the applied voltage, it is believed to react (with the use of the vanadium pentaoxide catalyst) according to the following reactions:



At the same time, O^{2-} is migrating to the anode 24 and leaves oxygen vacancies behind. Accordingly, the surface of V_2O_5 is full of oxygen vacancies and V^{+4} sites, which are very active for absorption and chemical reduction of NO_x .

Thus, the following reaction is believed to proceed:



That is, the adsorbed NO_x is believed to re-oxidize the reduced V^{+4} back to the original oxidation state.

-5-

The oxygen ions then migrate across the electrolyte membrane 22 and then are oxidized to elemental oxygen as follows:



The overall reaction is



For large scale removal of NO_x from a gas stream, a stack of the inventive electrochemical cells could be utilized.

The invention is not limited to use of the previously identified supported vanadium pentaoxide (V_2O_5) oxides as the cathode. Any oxide with the
10 following properties should be a suitable catalyst for this process:

(1) The oxide constitutes a redox couple, i.e., the oxide can be relatively easily reduced and, in turn, the reduced form can be easily re-oxidized back to the original oxidation state.

(2) During reduction of the oxide, oxygen vacancies are
15 simultaneously created and the reduced sites selectively adsorb NO_x .

In many cases, metal oxides in the reduced form absorb NO_x faster and stronger, as for instance on Cu^{+1} ions versus Cu^{+2} , Cr^{+2} ions vs. Cr^{+3} , Fe^{+2} vs. Fe^{+3} , and Mn^{+2} vs. Mn^{+4} .

Typical porous catalysts for use with the invention include:

20 $(\text{V}_2\text{O}_5)_x(\text{TiO}_2)_{1-x}$, $(\text{V}_2\text{O}_5)_x(\text{SiO}_2)_{1-x}$, NiO , SnO_2 , $(\text{V}_2\text{O}_5)_x(\gamma\text{-Al}_2\text{O}_3)_{1-x}$, CuO_2 , Fe_3O_4 , Nb_2O_5 , LCF (i.e. $\text{LaCu}_{1-x}\text{Fe}_x\text{O}_3$), $[(\text{Bi}_2\text{O}_3)_{1-x}(\text{Y}_2\text{O}_3)_x]_{1-k}(\text{LSCF})_k$, (i.e. $[(\text{Bi}_2\text{O}_3)_{1-x}(\text{Y}_2\text{O}_3)_x]_{1-k}(\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-y}\text{Fe}_y\text{O}_3)_k$), LSMCF (i.e. $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-y-z}\text{Cu}_y\text{Fe}_z\text{O}_3$), copper molybdenum sulfide ($\text{Cu}_{0.5 \text{ to } 1.85}\text{Mo}_6\text{S}_8$), and mixtures thereof, wherein x and y vary from 0.01 to 0.99 and k varies from 0 to 1.

25 Similarly, the invention is not limited to use of the above-mentioned Y_2O_3 -stabilized zirconia as the electrolyte. Numerous stabilized oxygen ion-conductive oxides may be employed as the solid electrolyte. These include, but are not limited to:

- (1) Ceria-based, e.g., $(\text{CeO}_2)_{1-a}(\text{CaO})_a$, $0.09 < a < 0.15$;
30 (2) Zirconia-based, e.g., $(\text{ZrO}_2)_{1-b}(\text{Yb}_2\text{O}_3)_b$, $0.07 < b < 0.12$; and
(3) Bismuthia-based, e.g., $(\text{Bi}_2\text{O}_3)_{1-a}(\text{Er}_2\text{O}_3)_a$, $0.09 < a < 0.15$.

-6-

Due to the high resistivity of the catalyst 26, a conductive layer is preferably employed on the top of the catalyst to enhance the overall conductivity of the electrochemical cell meanwhile maintaining the selective absorption of NO_x when other reducible gas species, particularly O_2 , are present in the gas stream.

In electrochemical process, noble metals such as platinum are generally used as electron collectors or electrodes. However, the catalytic reduction of NO_x on platinum group metals is markedly inhibited by O_2 in gas stream. This behavior has been attributed to preferential chemisorption of O_2 over NO_x on the platinum surface.

In the present invention, perovskites, e.g., lanthanum strontium manganate ("LSM" i.e. $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, $x=0.01-0.99$), which are chemically and thermally compatible with the catalyst 26 and the electrolyte membrane 22, may be employed. Considerable NO_x reduction (30%) has been achieved by this cell configuration at acceptable energy consumption levels.

Typical electron collecting layers are made from a material selected from the group consisting of LSM, LSMC (i.e. $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-y}\text{Co}_y\text{O}_3$), LSC (i.e. $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$), LSCF (i.e. $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$) -- wherein in these materials, x and y vary between 0.01 and 0.99 -- platinum, SrMnO_3 and mixtures thereof.

The unique advantages offered by these approaches include:

- (1) A decreased sensitivity to any O_2 present due to the unique electrochemical cell design. This advantage can be extremely important in applications such as for treating the exhaust of a diesel engine wherein 10 to 15% of the exhaust may be oxygen.
- (2) A chemical-reducing agent is not involved and hence the invention is highly desirable for mobile and small scale combustion sources. For example, no ammonia is present to be released with the exhaust gas (i.e. there is no "slip").
- (3) A high NO_x conversion is achieved with less energy consumption due to the electrochemically-enhanced catalytic activity of the catalysts. Furthermore no toxic N_2O is formed.

-7-

(4) A device utilizing the technology is compact and portable.

Analysis indicates that the device can be relatively small in size. Such a small size allows for both stationary and mobile applications. For especially stationary applications, the device can be used in combination with other technologies, e.g.

5 SCR as sequential filters.

(5) As demonstrated in the EXAMPLES, the cell operates at relatively low voltages, allowing typical mobile power sources (e.g. a generator/alternator or battery) to be used.

(6) For internal combustion applications, the presence of lead in the
10 gas stream will not poison the electrochemical cell.

The invention is further described by the following illustrative examples.

EXAMPLE I

A device such as that depicted in FIGs. 1 and 2 was made. The cell
15 structure consisted of a 0.5 mm thickness of hereinafter described materials for the solid oxide electrolyte, porous silver was used as the anode, vanadium pentaoxide was used as the porous cathode, LSM was used as the electron collecting layer, while platinum served as the porous metal grid.

20 1. Preparation of Electrolyte Materials

Three types of oxygen conductive solid electrolytes were prepared:

(1) fully-stabilized cubic $(\text{ZrO}_2)92\%(\text{Y}_2\text{O}_3)8\%$, (2) fully-stabilized cubic $(\text{ZrO}_2)91\%(\text{Y}_2\text{O}_3)4.5\%(\text{Yb}_2\text{O}_3)4.5\%$ and (3) $(\text{CeO}_2)85\%(\text{CaO})15\%$.

25 2. Catalyst preparation

2.1. Impregnation

Supported vanadia based catalysts were prepared by *impregnation* which is a procedure whereby a certain volume of solution containing a compound of vanadium is totally adsorbed into the pores of a support. Supports are used to
30 improve mechanical strength, thermal stability, lifetime, as well as selectivity and activity. Commercially available TiO_2 (Degussa P25) and $\gamma\text{-Al}_2\text{O}_3$ (Degussa) supports were used.

-8-

The support materials were first wetted with high purity distilled water and dried overnight in the 50 to 120°C temperature range. The desired amount of NH_4VO_3 was added to 1 to 10M oxalic acid solution, which on heating formed $(\text{NH}_4)_2[\text{VO}(\text{C}_2\text{O}_4)_2]$ complex. The solution was added to the support, and the water removed by evaporation with continuous stirring. The resulting solid was dried overnight at 50 to 120°C and was calcined in flowing air for a few hours in the 400 to 600°C temperature range. Designed vanadium contents were confirmed by Inductively Coupled Plasma Spectroscopy and X-ray diffraction. Surface areas were measured by BET method.

2.2. Solution Precipitation

The catalyst was also synthesized by solution precipitation techniques.

Ammonium vanadate (NH_4VO_3) was reacted with titanium tetrachloride (TiCl_4) in aqueous solution to form titanium vanadate precipitates. At the same time, titanium tetrachloride reacted with ammonium hydroxide (NH_4OH) in aqueous solution to form titanium hydroxide precipitates. After filtration and drying, the two precipitates (titanium vanadate and titanium hydroxide) were mixed with appropriate proportions and were calcined in a temperature range of 400 to 600°C for a few hours. The resulting powders were confirmed by Inductively Coupled Plasma Spectroscopy and X-ray diffraction.

3. Processing of Porous Cathode

Open porous catalysts were prepared as described as following:

- (1) The prepared catalysts were finely divided into small particles by ball milling;
- (2) The finely-divided particles, after drying, were then mixed with an appropriate organic binder in a suitable solvent to make a paste;
- (3) The paste was screen printed on one side on the electrolyte; and
- (4) The paste was dried at 50°C and fired in a temperature range between 400 to 550°C to burn off the organics and form an open porous catalyst.

4. Processing of Perovskites Conductive Layer

Due to the high resistivity of the vanadia-based catalyst, a conductive layer is preferably employed on the top of the catalyst to enhance the overall conductivity of the electrochemical cell meanwhile maintaining the selective absorption of NO_x when other reducible gas species, particularly O_2 , are present on the gas stream.

The Perovskites conductive materials, e.g., strontium doped lanthanum manganate, were synthesized by a gel resin process. In this process, soluble salts of the chemical constituents such as La, Mn, and Sr were dissolved in water. Citric acid and ethylene glycol were then added to this solution. An appropriate amount of citric acid was chosen so that four ligands were available to which the metal ions can attach. Ethylene glycol polymerized the citric acid by a slow and controlled drying process. The result amorphous mixture was then calcined to yield oxides which were then reactively calcined in air to give a homogeneously doped powder. The powder was then milled and sieved to achieve a uniform particle size. The phases of the powder were examined by X-ray diffraction.

5. Cell Fabrication

Flat-plate electrochemical cells were designed and fabricated for simplicity on construction and operation as well as accuracy in evaluation of the critical parameters. Fully-stabilized cubic zirconia electrolytes were used in this study.

The cathode of the cell was titania supported vanadia catalyst, which was applied on one side of the electrolyte disk. The Perovskite conductive layer was coated on the top of the vanadia layer. The anode of the cell was silver. All the coatings were screen-printed. The thickness of screen-printed Ag, V_2O_5 , and Perovskites coatings is approximately 20 microns.

To improve the adherence of the catalyst film on tape-casted ZrO_2 pellets, the pellet surfaces were roughened by adding a slurry containing fine (1-2 μm) ZrO_2 powder, followed by drying and firing at 1500°C.

-10-

Both cathode and anode were mechanically bonded with two platinum grids, which were connected to two silver wires, acting as electrical leads.

6. Characterization of Electrochemical Cells

5 Four-point and two-point impedance spectroscopy was extensively used to characterize the electrical properties of impedance response of each individual component of the cells, such as electrolyte, electrode, and catalyst, as well as the electrochemical systems. The phase composition of various materials were investigated using X-ray diffraction.

10 Fabricated cells were examined by potential sweep techniques to ensure that the cells made were functioning electrochemically. In case of high internal resistance, the cell was diagnosed by impedance spectroscopy to resolve the electrolyte resistance from the interfacial resistance, identifying the source of high impedance.

15

7. Analysis of Gases

The catalytic tests of NO_x reduction of the electrochemical cell was carried out in the experimental apparatus sketched in FIG. 2. Three gas lines carrying NO_x/N_2 , O_2 and N_2 respectively, allow for adjustments in the concentration and flow rate of NO_x , O_2 and N_2 . The reaction temperature, measured by a chromel-alumel thermocouple, was controlled in the range between 300 to 500°C. The NO_x and O_2 concentrations were measured by a HP 5890 chromatography equipped with a Haysep "D" 9.14 meter (30 foot) packed column, and a UTI Quadrupole Mass Spectrometer before and after the voltage was applied. A commercially available NO sensor (EIT) and O_2 sensor (Ceramatec) was also connected in the gas line to confirm the NO_x and O_2 concentration. Applied voltage was supplied from a constant potential source ranging from 0 to 5 volts. The NO_x conversion efficiency was calculated based on the NO_x concentration changes before and after the voltage was applied.

30

-11-

8. Effect of Increasing Voltage when Gas Contained Low Concentration of O₂

Fifty cc per minute of a gas was passed through the gas inlet of the device at a temperature of 350°C. The gas contained 600 ppm NO and 2000 ppm oxygen. A DC voltage was applied across the electrochemical cell and was steadily increased from 0 to 5 volts. The amount of NO conversion at each voltage is displayed graphically in FIG. 3. This graph shows that the reduction of NO_x is an electrochemically activated process, as indicated by the shape of the conversion curve as a function of the applied voltage. When the applied voltage is lower than the theoretical reduction potential of V₊₃ to V₊₄, the conversion efficiency is negligible. As the applied voltage exceeds the theoretical reduction potential of V₊₃, the conversion efficiency rapidly increases with the increase of the applied voltage up to the point, where the applied voltage is sufficiently high to reduce all available NO_x. Thereafter, the conversion efficiency becomes relatively independent of the applied voltage.

9. Power Consumption at Various Voltages when Gas Contained Low Concentration of O₂

The power consumption in brake horsepower-hours (BHH or BHpHr) per gram of NO_x for the experiment of EXAMPLE 1.8 was measured. The results are graphically depicted in FIG. 4. As can be deduced from FIGS. 3 and 4, from an efficient power consumption point of view, the system is preferably operated at a voltage of less than 3 volts DC.

10. Effect of Increasing Voltage when Gas Contained High Concentration of O₂

The experiment of EXAMPLE 1.8. was repeated at various oxygen concentrations. FIG. 5 represents NO_x conversion efficiency under 7 and 15% oxygen containing gases. The NO_x conversion efficiency increases with the increase of the applied voltage above 0.5 volts. The figure also indicates that oxygen is a strong competing species during the NO_x reduction process.

11. Power Consumption as a Function of O₂ Concentration

FIG. 6 shows the power consumption of the electrochemical cell at various O₂ concentrations under three applied voltages. The arrow on the graph indicates that 0.02 BHpHr/gram of NO_x is equivalent to 4% of total engine power of a 400 horse-power engine.

12. Effect of Gas Temperatures

Thirty cc per minute of a gas was passed through the gas inlet of the device. The gas contained 550 ppm NO; 6.2% oxygen, with a balance of nitrogen at a constant DC voltage of 2 volts applied across the electrolyte.

The temperature was increased from 350 to 430°C while the percentage NO conversion was measured. The amount of NO conversion at varying gas temperatures is displayed graphically in FIG. 8.

As demonstrated by FIG. 8, operation of this particular system at a temperature higher than about 400°C is not advisable evidently due to the considerable portion of the energy being consumed in the transport of oxygen through the electrolyte at such high temperature.

EXAMPLE II

Based on the data available, the approximate size of the devices for diesel engines was estimated as follows:

Condition: Exhaust flow from diesel engines is 5.5 kg/min. with 280 ppm NO, 14 ppm NO₂, and 28 ppm SO₂

Case I: 100% Electrochemical Reduction

In this case, it is assumed that (i) no chemical decomposition of NO_x and SO_x occurs, i.e., the oxides of nitrogen and sulfur are electrochemically decomposed and hence all the oxygen ions are pumped through the electrolyte, and (ii) there is no electrochemical reduction of other reducible species (O₂, H₂O, CO) due to the selective adsorption of NO_x on TiO₂/V₂O₅ catalysts.

-13-

The oxygen-ion molar flux can be expressed as

$$N_{O_2} = \left(\frac{5.5 \text{ kg}}{\text{min.}} \right) \left(\frac{(1)(2.8 \times 10^{-4})}{(30)} + \frac{(2)(1.4 \times 10^{-5})}{(46)} + \frac{(2)(2.8 \times 10^{-5})}{(64)} \right)$$

$$= 589.31 \times 10^{-4} \text{ mol./min.} = 9.822 \times 10^{-4} \text{ mol./sec.}$$

The current required can be expressed as

5 $I = 189.53 \text{ (A)}$

Assuming that the operating current density is 200 mA/cm², which has been demonstrated for over 3000 hours for other oxygen-ion related devices, the surface area required to deliver 189.53 A current is 947.65 cm². This can be easily achieved by stacking 40 flat-plate electrochemical cells, each having a
10 surface area of 25 cm². The multilayer-stacking technology is established for fuel cells. Thus, the device will preferably have dimensions of 6.4 cm X 6.4 cm X 20.3 cm.

Case II: 100% Chemical Reduction

In this case, it is assumed that all of the NO_x and SO_x is chemically
15 decomposed at the catalysts and there is no electrochemical reduction of NO_x and hence there is no required current at all. Thus, the cathodes can be made in open porous form with effective surface area of several m²/gram and the functional unit of the system is potentially small in size.

In reality, however, the electrochemical reduction and the
20 electrochemically-induced chemical reaction will occur simultaneously. Thus, the actual current and hence the surface area required for the removal of NO_x will be much smaller than the numbers estimated in Case I. Accordingly, in theory, the dimension of a device should be somewhere between the sizes estimated in Case I and Case II.

25

EXAMPLE III

Estimation of Power Consumption

Condition: NO_x discharge rate from diesel engines is 4.5 g/hp-hr;

-14-

Assumption: 100% electrochemical reduction, i.e., all oxygen anions decomposed from NO_x will be pumped through the electrolyte and there is no chemical decomposition.

Estimation:

$$\frac{(4.5)}{(30)} (2)(96,485)(\text{Coulombs}) / 2,684,520(\text{watts} \cdot \text{sec})$$

$$= 0.01078 (\text{Coulomb/Watt-sec})$$

Applied Voltage (V)	Power Consumption (%)		
	100% Removal	80% Removal	65% Removal
1	1.08	0.86	0.70
0.9	0.97	0.78	0.63
0.8	0.86	0.69	0.56
0.7	0.75	0.60	0.49
0.6	0.65	0.52	0.42
0.5	0.54	0.43	0.35
0.4	0.43	0.34	0.28
0.3	0.32	0.26	0.21

For the electrochemically-catalyzed chemical reduction process, however, there is virtually no power consumption in the ideal case. Therefore the power consumption should range from 0 to about 1% of power output, depending on how much of the NO_x or SO_x is decomposed chemically rather than electrochemically. For 65% removal of NO_x and SO_x , the power consumption should be less than 0.7% of the power output.

Although the invention has been described with regard to certain preferred embodiments, the scope of the invention is to be defined by the appended claims.

-15-

CLAIMSWhat is claimed is:

1. An electrochemical cell for reduction of NOx comprising:
 - 5 (a) a solid electrolyte having sides;
 - (b) an anode on one side of the solid electrolyte;
 - (c) two layers on the side of the solid electrolyte opposite that of the anode, one of said layers is a porous catalyst, and the other layer is an electron conducting layer; and
 - 10 (d) a circuit that applies a potential across said anode and either said porous catalyst or said electron conducting layer.
2. The electrochemical cell of claim 1, wherein said electron collecting layer is made from a material selected from the group consisting of
15 lanthanum strontium manganate, lanthanum strontium manganese cobalt oxide, lanthanum strontium cobalt oxide, lanthanum strontium cobalt ferrite, platinum and mixtures thereof.
3. The electrochemical cell of claim 1, wherein said porous catalyst
20 is selected from the group consisting of $(V_2O_5)_x(TiO_2)_{1-x}$, $(V_2O_5)_x(SiO_2)_{1-x}$, $(V_2O_5)_x(\gamma-Al_2O_3)_{1-x}$, Cu_2O , SnO_2 , NiO , Fe_3O_4 , Nb_2O_5 , lanthanum copper ferrite, lanthanum strontium manganese cupric ferrite, copper molybdenum sulfide, and mixtures thereof, wherein x is 0.01 to 0.99.
- 25 4. The electrochemical cell of claim 1, wherein said electron collecting layer is sandwiched between the solid electrolyte and the porous catalyst, and serves as a cathode.
5. The electrochemical cell of claim 1, wherein said porous catalyst
30 is sandwiched between the solid electrolyte and the electron collecting layer, and serves as a cathode.

-16-

6. An electrochemical cell for nitrogen oxide reduction comprising:
a solid electrolyte having sides;
a metallic anode positioned on one side of said solid electrolyte;
a cathode positioned on the side of the solid electrolyte opposite that of the
5 metallic anode, said cathode comprising a porous gas-diffusion catalyst;
and
a conductive layer positioned on the cathode to enhance the conductivity of the
electrochemical cell and maintain the selective absorption of nitrogen
oxide.
- 10 7. The electrochemical cell of claim 6, wherein said solid electrolyte
is selected from the group consisting of an yttria-stabilized zirconia, stabilized
zirconia, stabilized bismuth oxide, stabilized ceria, and mixtures thereof.
- 15 8. The electrochemical cell of claim 6, wherein said conductive layer
comprises a perovskite oxide.
9. The electrochemical cell of claim 8, wherein said cathode is
nonstoichiometric vanadium oxide.
- 20 10. The electrochemical cell of claim 6, wherein said anode is silver.
11. A device for the electrochemical reduction of NO_x comprising:
(a) a container;
25 (b) an electrochemical cell, contained within said container, said electrochemical
cell comprising:
(i) a solid electrolyte having sides,
(ii) a metallic anode positioned on one side of said solid electrolyte,
(iii) a cathode positioned on the side of the solid electrolyte opposite that
30 of the metallic anode, said cathode comprising a porous
gas-diffusion catalyst, and

-17-

(iv) a conductive layer positioned on the catalyst to enhance the conductivity of the electrochemical cell and maintain the selective absorption of nitrogen oxide;

5 (c) a gas inlet leading into said container, said gas inlet directed to the electrochemical cell;

(d) a porous metal grid surrounding said electrochemical cell;

(e) a power source for electrifying said porous metal grid and said cathode; and

(f) a gas outlet for removing gas from said container.

10 12. A method of reducing NO_x in a gas stream comprising:
passing said gas stream by an electrochemical cell of any of claims 1 to 10.

13. The method according to claim 12, wherein the gas stream has a temperature of between 350 and 450 centigrade.

15 14. The method according to claim 12, wherein the gas stream further includes oxygen.

20 15. The method according to claim 12, wherein the potential applied to the electrochemical cell is direct current.

16. The method according to claim 14, wherein greater than 8% of the NO_x is converted to oxygen and nitrogen.

1/3

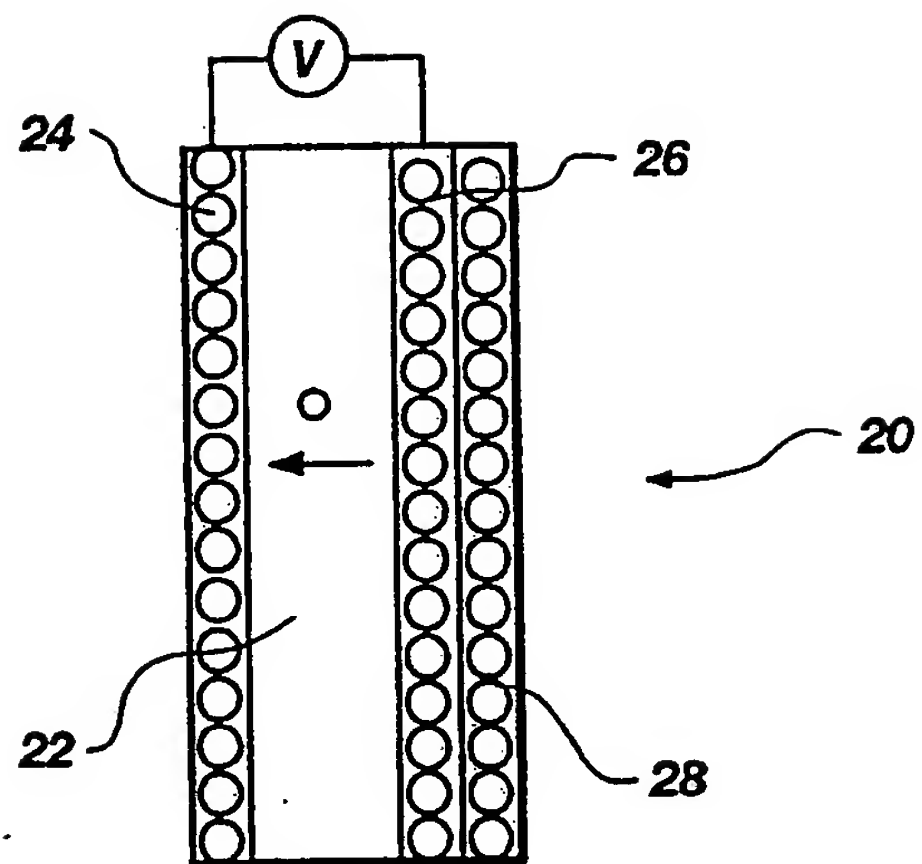


Fig. 1

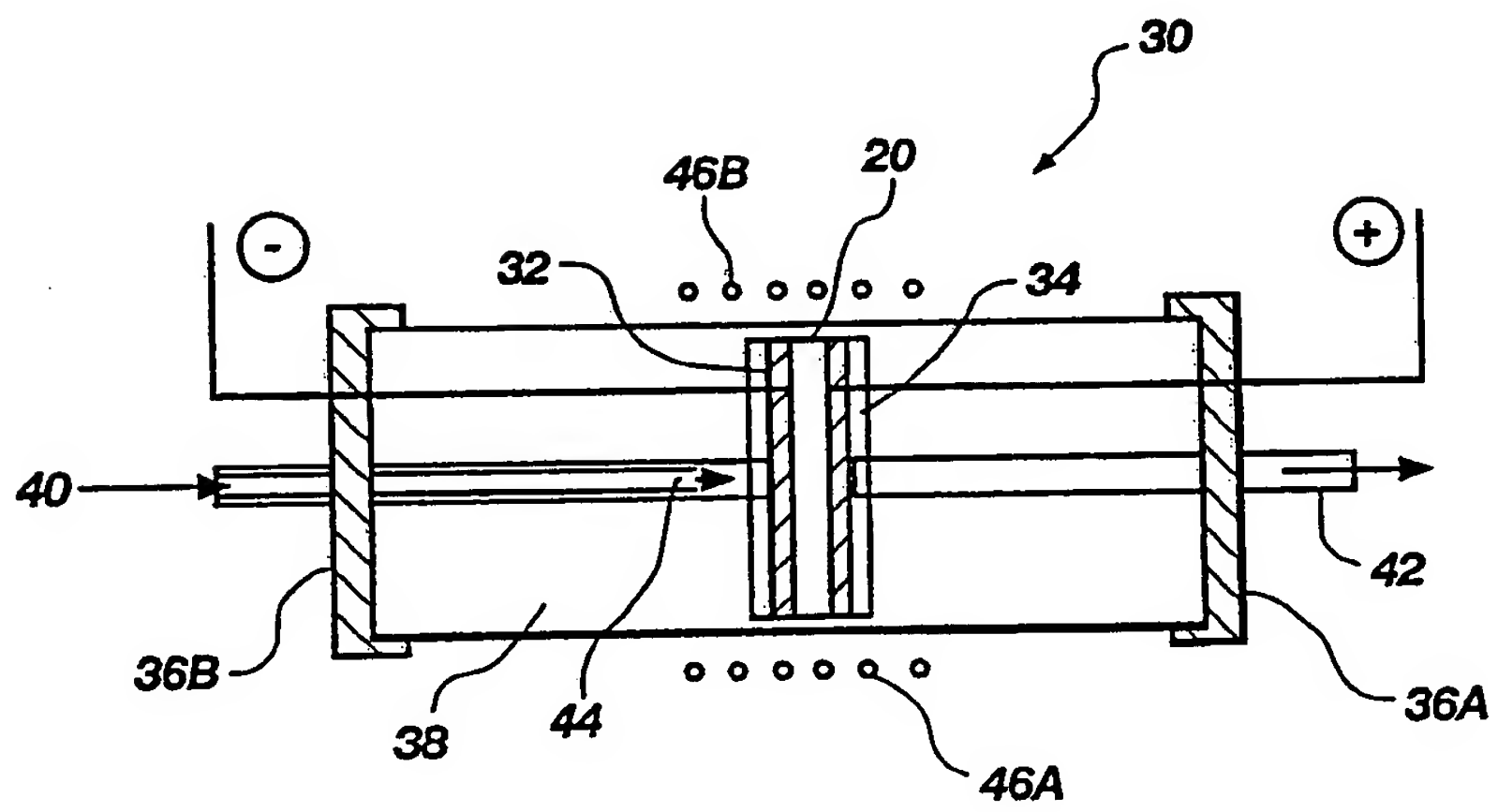


Fig. 2

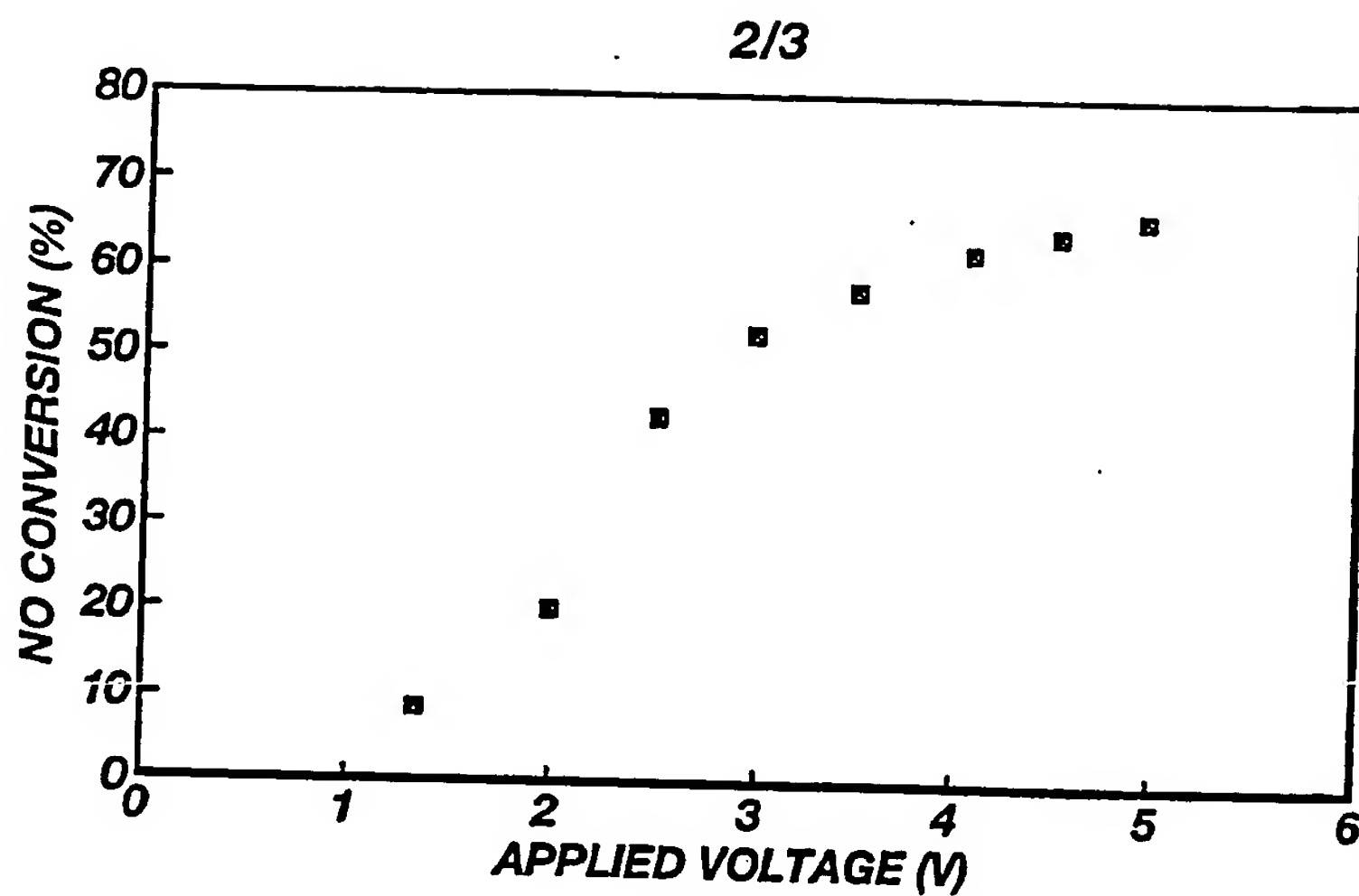


Fig. 3

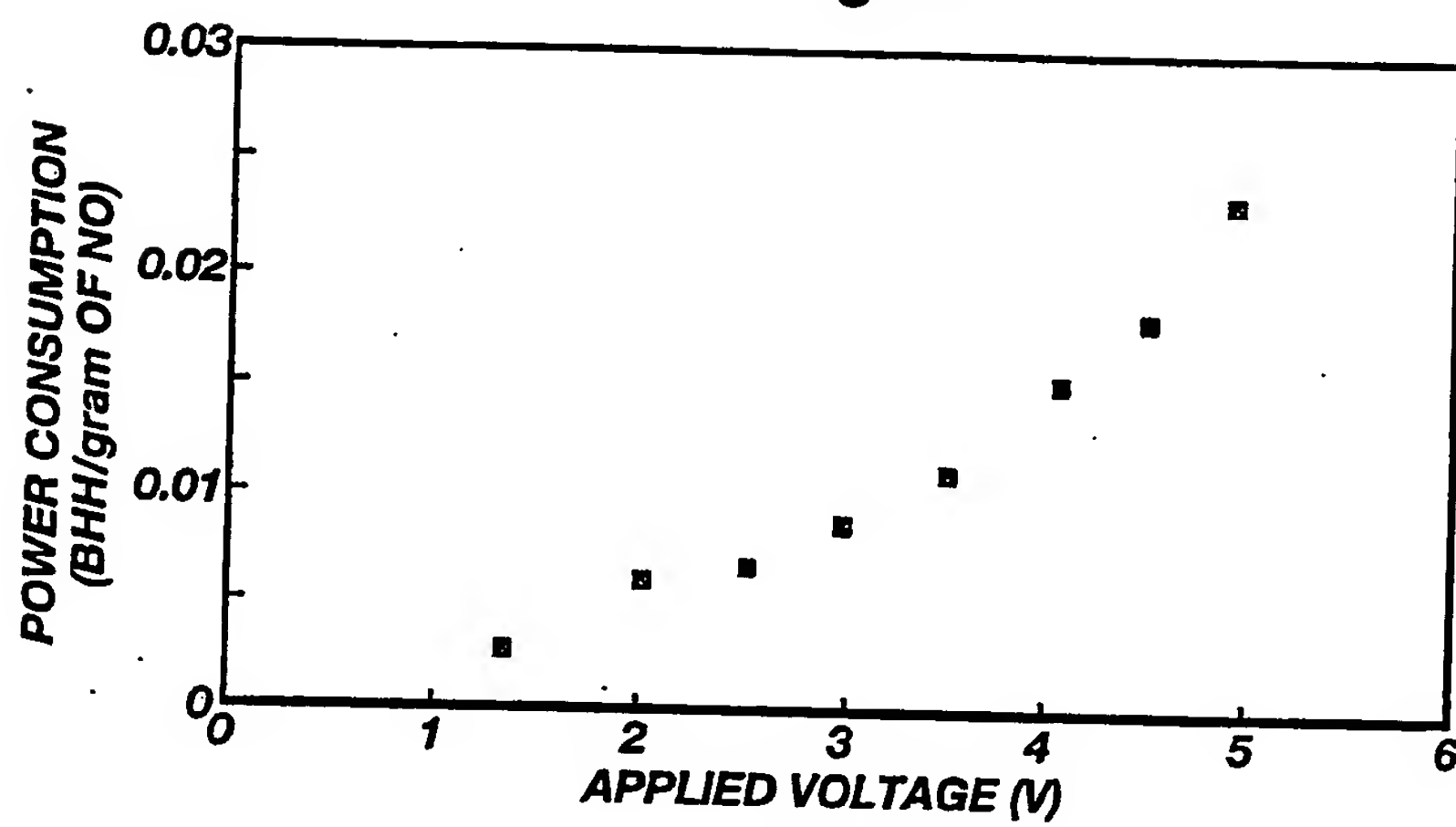


Fig. 4

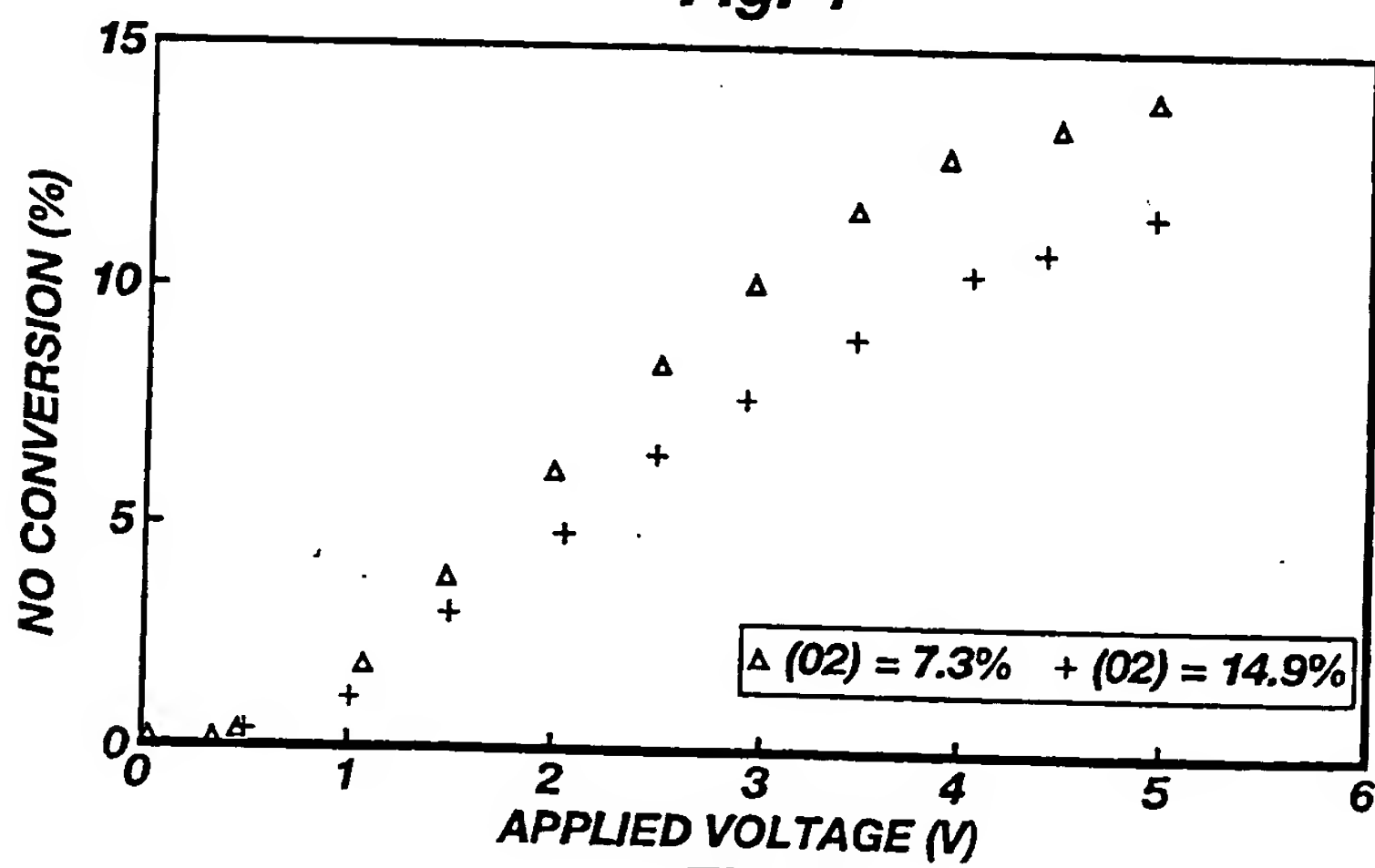


Fig. 5

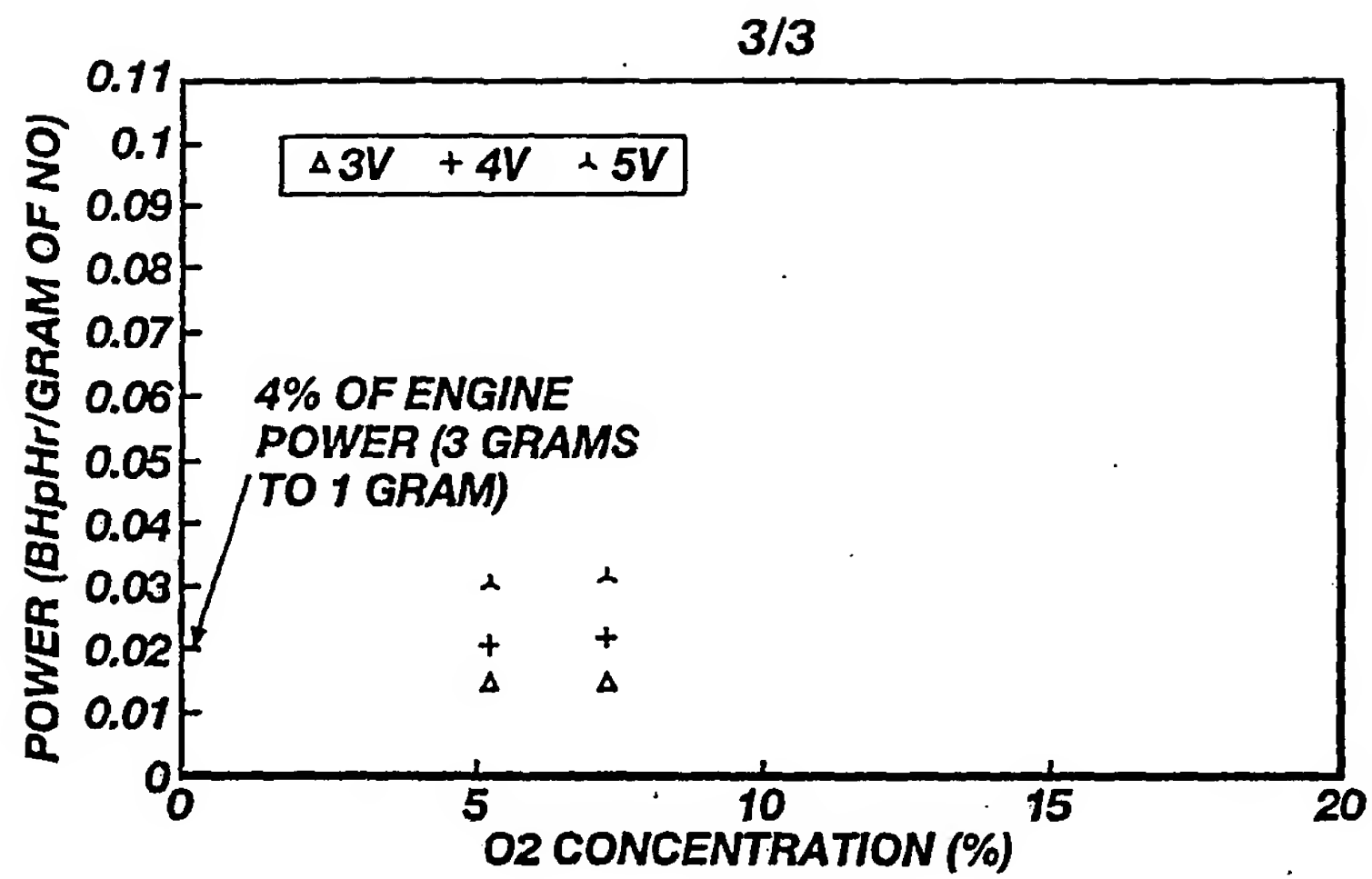


Fig. 6

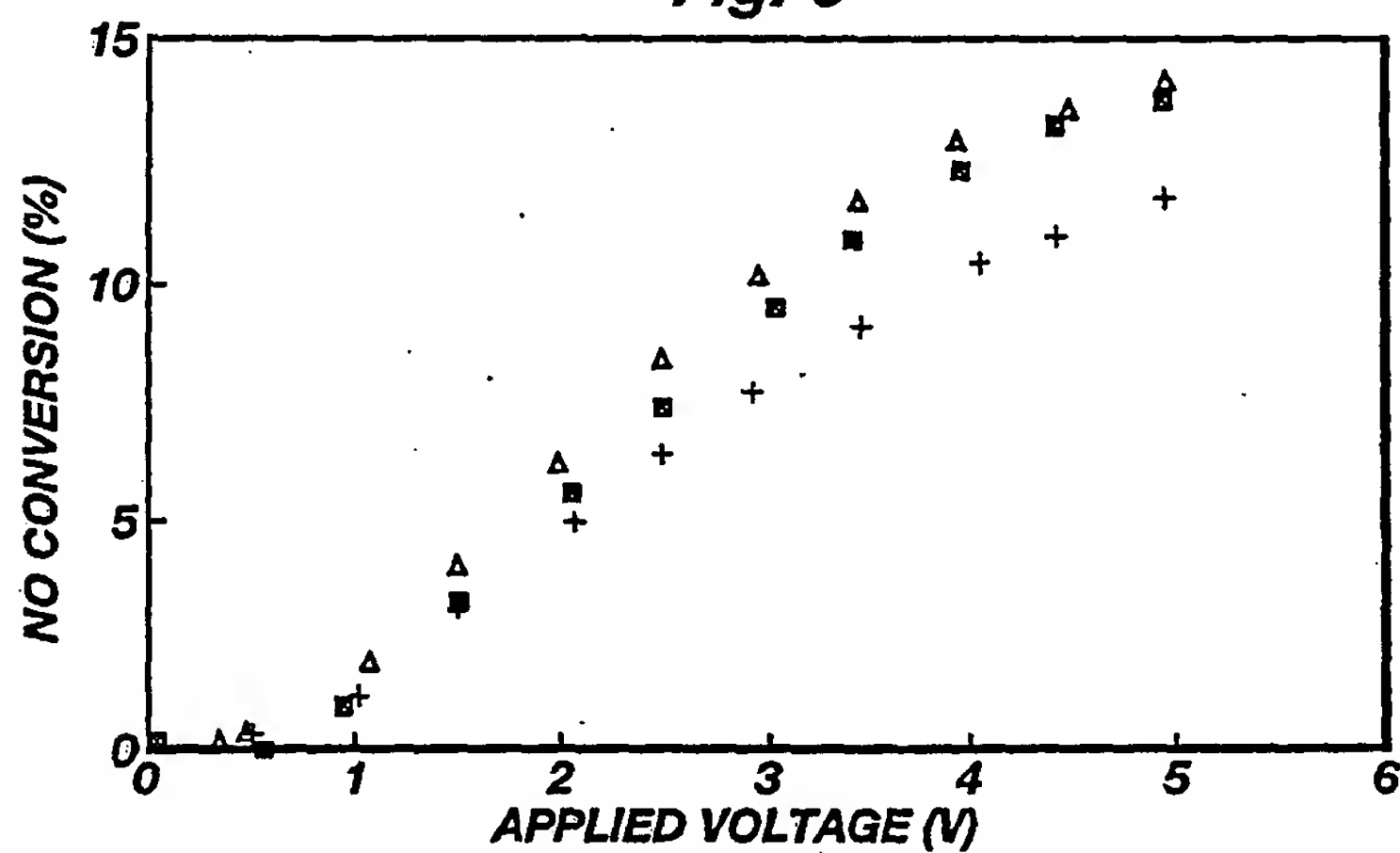


Fig. 7

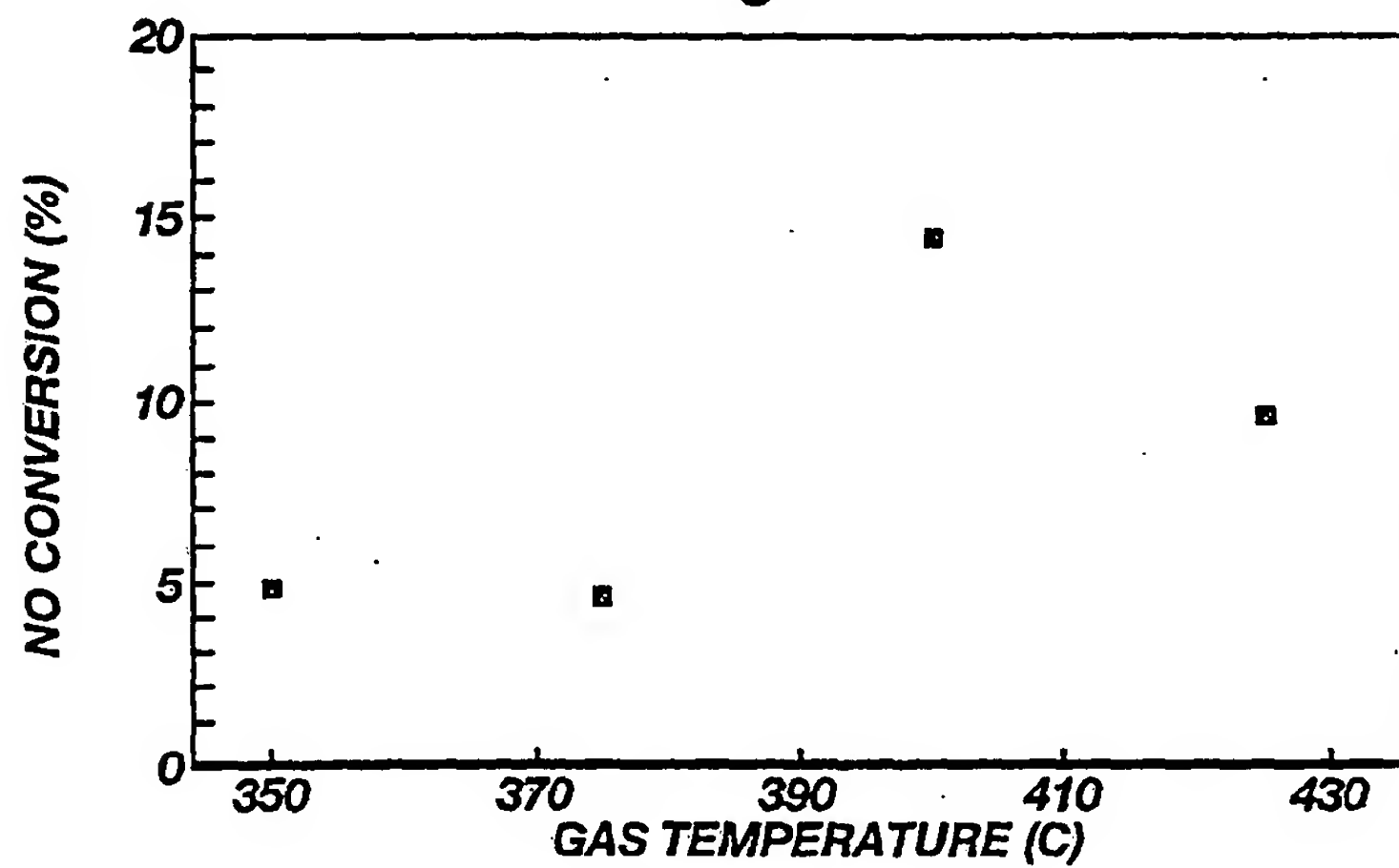


Fig. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/04525

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : Please See Extra Sheet.

US CL : 204/59R, 252, 265, 266, 295, 290R, 291, 292, 424, 426, 431

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X <u>Y</u>	US, A, 4,199,425 (Sinkevitch) 22 April 1980, Figs. 1 and 2, abstract; col. 2, lines 56-68; and col. 4, lines 9-40.	1-2, 4-7, 10 ----- 2-5
X <u>Y</u>	US, A, 4,253,925 (Mason) 03 March 1981, abstract; col. 2, lines 50-68; and col. 3, lines 44-49.	12-15 ----- 12-15
Y	US, A, 5,034,112 (Murase et al.) 23 July, 1991, col. 13, lines 28-35 and lines 60-63.	3, 8-11, and 20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A		document defining the general state of the art which is not considered to be of particular relevance
* E		earlier document published on or after the international filing date
* L		document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
* O		document referring to an oral disclosure, use, exhibition or other means
* P		document published prior to the international filing date but later than the priority date claimed
	* X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
	* Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
	* &	document member of the same patent family

Date of the actual completion of the international search

10 June 1994

Date of mailing of the international search report

23 JUN 1994

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. NOT APPLICABLE

Authorized officer

KATHRYN GORGOS

Telephone No. (703) 308-3328

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/04525

A. CLASSIFICATION OF SUBJECT MATTER:
IPC (5):

C25B 1/00, 02, 9/00, 11/00, 11/02, 11/04, 11/06, 11/08, 13/04; G01N 27/26

B. FIELDS SEARCHED

Minimum documentation searched

Classification System: U.S.

204/59R, 128, 129, 252, 265, 266, 295, 290R, 291, 292, 424, 426, 431

IPC (5): C25B 1/00, 1/02, 9/00, 11/00, 11/02, 11/04, 11/06, 11/08, 13/04

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS: NO_x or nitrogen oxide; solid electrolyte# or oxide electrolyt?; vanadium pentoxide or (copper or cu or tin or sn or nickle or ni or iron or fe or niobium or nb) and oxide#; LSM or LSMC or LSC or platinum or pt; zirconia of ceria or bismuthia; silver or ag

===== WPI =====

TI - Gas separation filter suitable for selectively separating acidic gases such as carbon dioxide and nitrogen oxides

AB - JP2000279773 NOVELTY - Gas separation filter consisting of a porous support and a separation film which is formed on at least one surface of the porous support, has gas permeability, and consists of an amorphous oxide having more than one pore formed by cyclic siloxane bonds is characterized in that functional groups containing nitrogen and silicon are bound, via oxygen, to a part of side chains of silicon in the cyclic siloxane bonds forming more than one pore.

- USE - The gas separation filter can be used for selectively separating acidic gases such as carbon dioxide and nitrogen oxides from gas mixtures.

- ADVANTAGE - The gas separation filter has high heat resistance and corrosion resistance.

- (Dwg.0/3)

PN - JP2000279773 A 20001010 DW200104 B01D71/70 013pp

PR - JP19990091779 19990331

PA - (KYOC) KYOCERA CORP

MC - A06-A00E2 A12-H04 E11-Q01 E31-H02 E31-H04 E31-N05C J01-E03E

DC - A26 A88 E36 J01

IC - B01D67/00 ;B01D71/70

AN - 2001-027457 [04]

===== PAJ =====

TI - GAS SEPARATION FILTER AND ITS PRODUCTION

AB - PROBLEM TO BE SOLVED: To improve the permeation rate of acidic gas, to assure excellent corrosion resistance, heat resistance and water resistance and to improve a separation characteristic by coupling a functional group containing nitrogen having basicity and silicon to the side chain of Si existing within the pores of a siloxane bond forming the pores of a separation membrane.

- SOLUTION: The gas separation filter 1 consists of a porous support 2 and the separation membrane 3 which is formed on its one surface and consists of an amorphous oxide containing Si having the plural pores 4. In the meantime, the separation membrane 3 basically consists of the amorphous oxide having the pores 4 formed by the cyclic siloxane bond expressed by -Si-O-. The functional group containing the nitrogen (N) and the silicon (Si) is bonded to the side chain of part of Si existing within at least the pores 4. More specific, the functional group expressed by the formula is usable as the functional group containing the nitrogen (N) and the silicon (Si). Since the functional group exhibits the basicity, the separation of the acidic gas is made possible.

PN - JP2000279773 A 20001010

PD - 2000-10-10

ABD - 20010205

ABV - 200013

AP - JP19990091779 19990331

PA - KYOCERA CORP

IN - OSHIMA HITOHIDE;SEKI YOUJI

I - B01D71/70 ;B01D67/00

